SAND2013-7067C

The Influence of CO_2 on Oxy-fuel Combustion of Pulverized Coal

Christopher Shaddix, Ethan Hecht, Manfred Geier
Sandia National Laboratories
Livermore, CA 94550

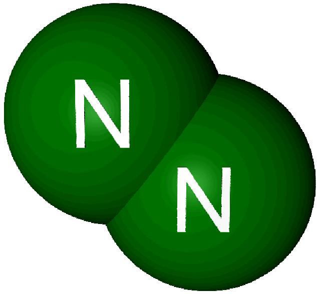
and

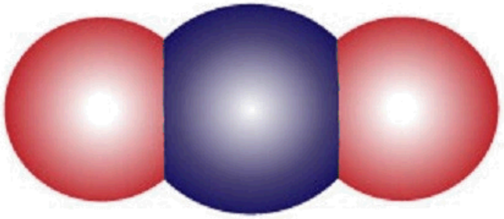
Alejandro Molina
Universidad Nacional de Colombia-Sede Medellín
Medellín, Colombia

3rd Oxyfuel Combustion Conference
Ponferrada, Spain
Sept. 9-13, 2013

Motivation for this talk:
Confusion over Effects of CO_2 in Oxy-fuel Combustion

- How does replacing this with this affect PC combustion?





O=C=O

- Important to understand differences in **fundamental properties** and then *propagate* understanding to **observed effects**

. . . else risk possible improper interpretation of observations

CO_2 vs N_2, on molecular scale

- CO_2 has much higher mass (44 amu vs. 28 amu)
- CO_2 is slightly larger (collisional diameter of 390 vs. 375 x 10^{-12} m)
- CO_2 is heteronuclear, triatomic molecule (IR-active rotational-vibrational energy states)
- CO_2 is more reactive (BDE of 532 kJ/mol vs. 945 kJ/mol)

Effect #1: C_p

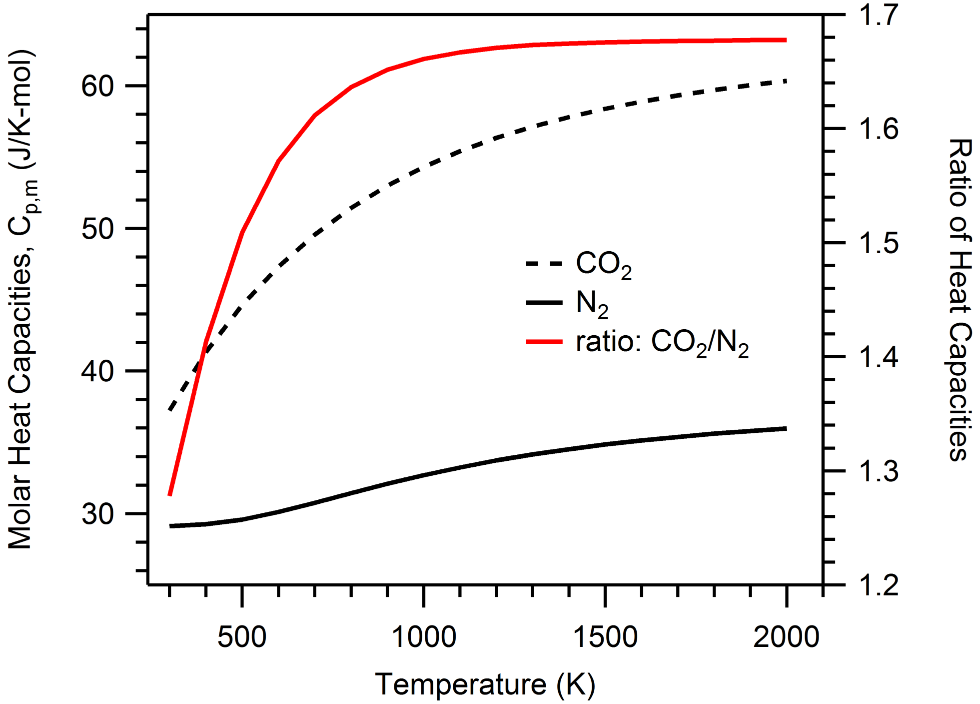
- Heat capacity on a molar basis is the relevant factor for gas-phase processes (gas number density is independent of molecular mass)

- Additional vibrational and rotational degrees of freedom for atomic motion result in greater heat capacity for CO_2, on molar basis

$$C_{p,m} = C_{v,m} + R = \frac{(f+2)}{2} R$$, where f = # deg of freedom

- As temperature increases, more degrees of freedom are activated in CO_2, giving an increasing heat capacity, relative to N_2, until all 13 dof are activated (vs. 7 for N_2)

Effect #1: C_p



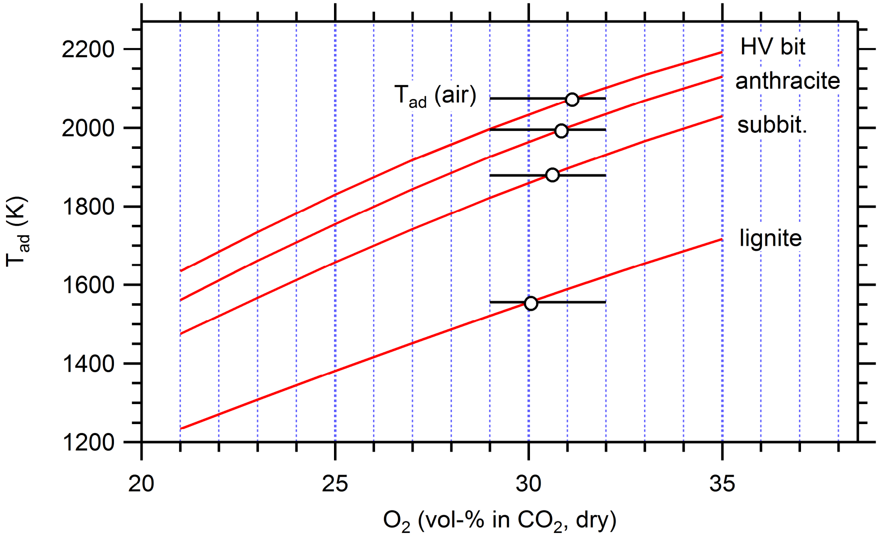
At high temperatures (> 1000 K), molar C_p of CO_2 is ≈ **1.67x** that of N_2

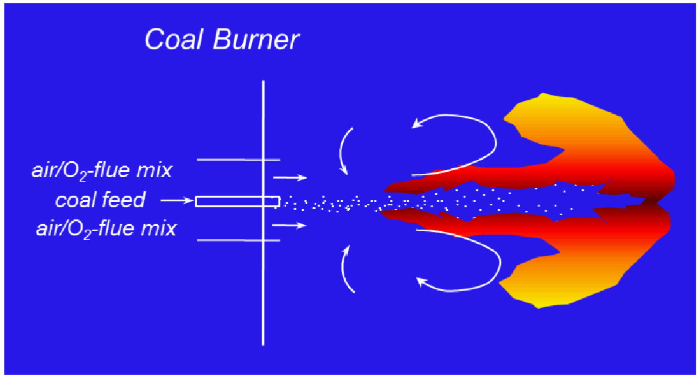
Note: because the MW_{CO2} is 1.56x MW_{N2}, at high T the *specific* heat of CO_2 is just slightly higher than specific heat of N_2

Effects of a higher molar C_p for CO_2

High C_p means a given amount of energy release or energy transfer results in a smaller temperature rise, so . . .

- With oxy-fuel combustion, burners/boilers need to be operated with less diluent to achieve similar temperatures as combustion in air





  - flame holding (i.e. burner stability) is very sensitive to combustion product temperature

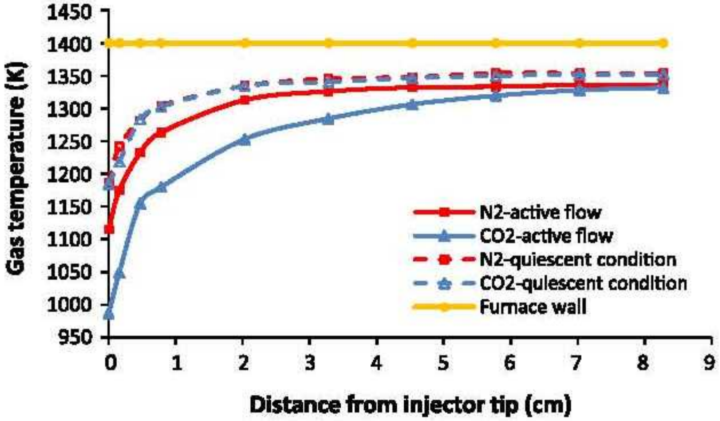
Effects of a higher molar C_p for CO_2

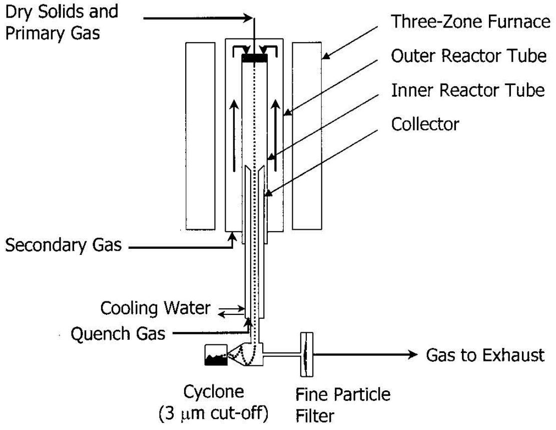
High C_p means a given amount of energy release or energy transfer results in a smaller temperature rise, so . . .

- Lower diluent flow means lower gas velocities (increasing residence time, altering distribution of radiant vs convective heat transfer, affecting turbulent flow characteristics)
- Delivering coal to a furnace with cool CO_2 has strong impact on coal stream heat-up and ignition (particularly in laminar flow)

Measured temperatures for drop tube ignition experiments

(Khatami, Stivers, and Levendis, CNF 159:3554-3568, 2012)





Not an effect of the higher molar C_p of CO_2

For most pc particles (< 70 μm in diameter), char oxidation rate is governed by a balance of oxygen diffusion to the particle, chemical reaction, and radiant and convective heat transfer from the particle (single-film model)

$$\underbrace{\frac{d_p \rho_p C_{p_p}}{6}\frac{dT_p}{dz}}_{\textbf{thermal inertia}} = \underbrace{-\varepsilon\sigma\left(T_p^4 - T_w^4\right)}_{\textbf{radiant loss}} \underbrace{-\frac{2\lambda}{d_p}\left[\frac{\kappa/2}{e^{\kappa/2}-1}\right]\left(T_p - T_g\right)}_{\textbf{convective loss}} + \underbrace{q\Delta h}_{\textbf{heat release}}$$

- no dependence of C_p for these processes (during steady state)
- thermal conductivity (λ) of surrounding gas is only thermal property that is important
- only for cases where CO oxidation in boundary layer is important (larger particles and high gas T or high O_2 concentration) should C_p play a role

Effect #2: Thermal Radiation

- N_2 has negligible thermal radiation, because only highly excited molecules can radiate, mostly at blue-violet or UV wavelengths (no lower energy rotational-vibrational transitions in IR)
- CO_2 thermal radiation (and radiation absorption) is significant at boiler length scales
- Combined influence of lower gas velocities (≈ 15% lower) and contribution of radiation from CO_2 results in pilot-scale and demo-scale furnaces operating with 27 – 28 % O_2 to match radiant heat transfer with air-fired combustion, rather than 30 – 31% O_2 needed to match actual flame temperatures

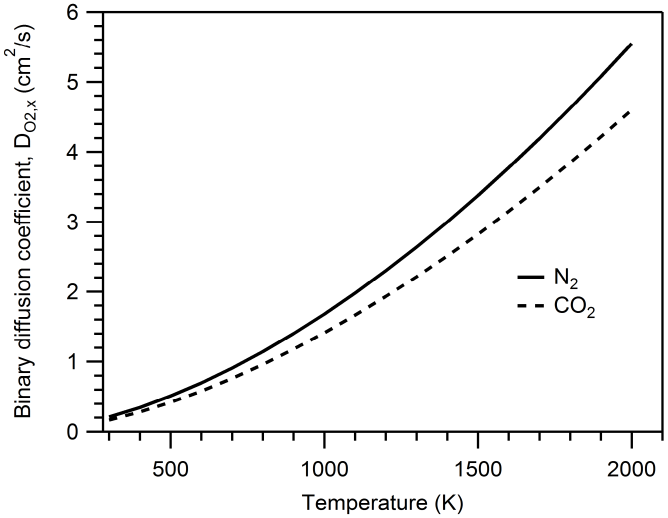
Effect #3: Gas Diffusion

- From dilute gas theory, bimolecular gas diffusivity follows

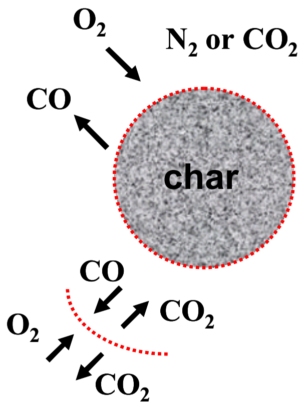
$$D_{a,b} \propto \sqrt{\frac{1}{m_a}+\frac{1}{m_b}} \cdot \frac{T^{3/2}}{P(d_a+d_b)^2}$$

- Larger collision diameter and mass (especially), decreases diffusion of molecules through CO_2

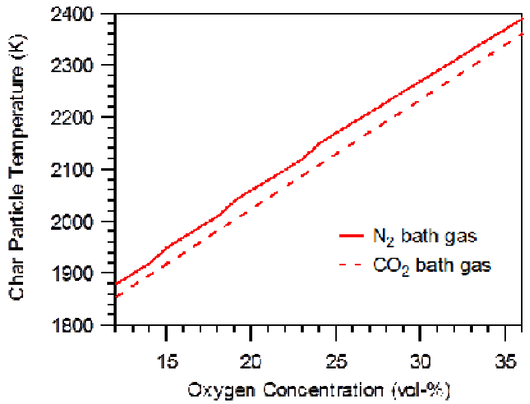
- For most molecules of interest (including O_2) diffusivity in CO_2 is ≈ 17% lower than diffusivity in N_2

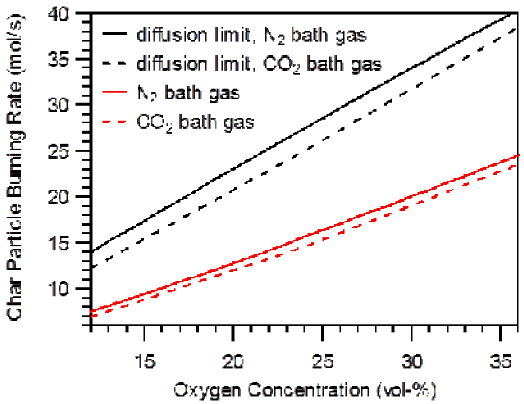


Effects of a lower diffusivity in CO_2



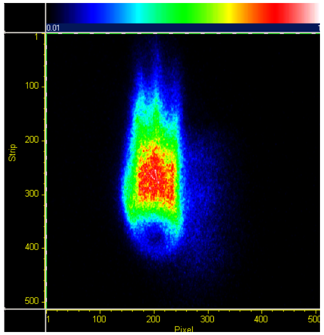
- For all but zone I (kinetically controlled) combustion, the char oxidation rate depends on O_2 diffusivity
  - for a 100 μm dia. hv bit. char particle, calculated effect of reduced diffusivity is to reduce char T by 40 K and burning rate by 7%





- Diffusion rate of CO away from char particle also affected, impacting boundary layer oxidation of CO

- For particle(s) burning with an envelope flame, reduced O_2 and volatile diffusivity reduces burning rate



Effect #4: Heterogeneous Reactions

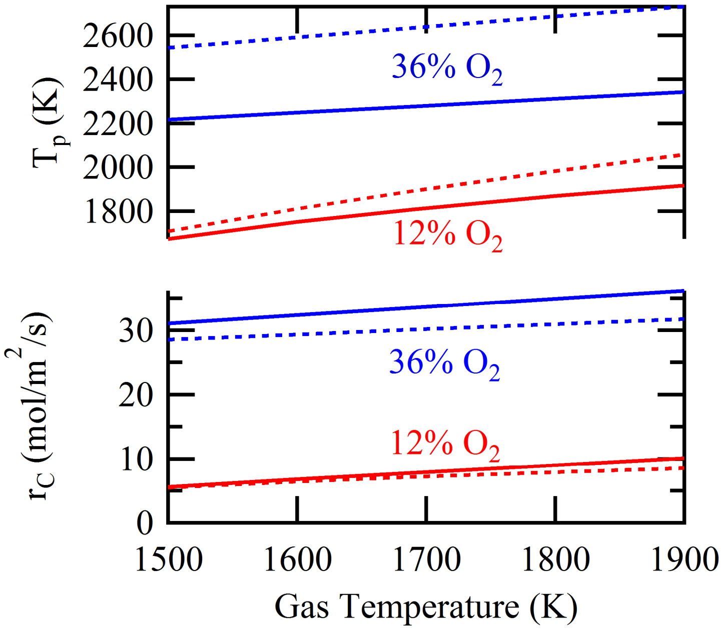
- Much confusion over role of CO_2 gasification reaction, and its effect on devolatilization and char conversion
- At low to intermediate temperatures, where char devolatilization occurs, gasification rate is extremely slow – irrelevant over timescales of interest for combustion
- Because the activation energy of CO_2 gasification reaction is large (≈ 250 kJ/mol), it becomes increasingly important at high T
- At 2000 K, the kinetic rate coefficient for CO_2 gasification is still ≈ 100x slower than oxidation, but larger CO_2 concentration, greater penetration of particle, and large *endo*thermicity of reaction make it important $CO_2 + C(s) \rightarrow 2CO \quad (\Delta H_{rxn} = +172\, kJ/mol_C)$

Effects of Char Gasification Reaction

- Endothermicity of reaction decreases char temperature substantially (at high temperatures, where gasification is active)

- Reduction in char temperature reduces char oxidation rate – almost completely offsetting the added char consumption from gasification

Simulation results: 100 μm subbit. char particle burning in O_2/CO_2 mixtures
(Hecht et al., CNF 159:3437-3447, 2012)



dashed lines: ignoring gasification rxns

solid lines: including gasification rxns

Effect #5: Gas-Phase Reactions

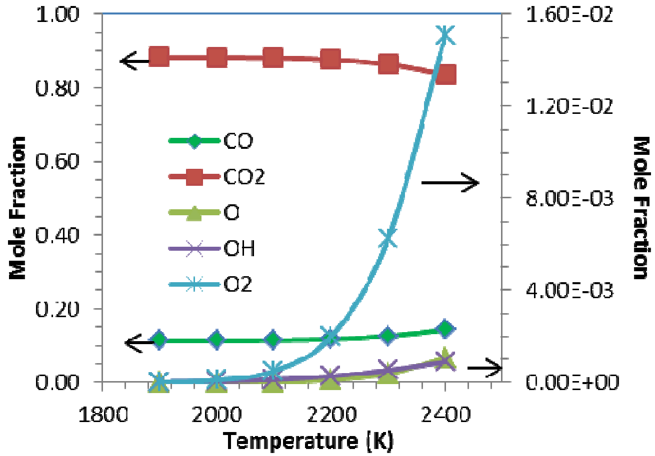
- Gas-phase reactions with CO_2 are often forgotten, but are significant in the flame zone

- Several kinetic studies have demonstrated that

$$H + CO_2 \rightarrow CO + OH$$

is important during oxy-fuel combustion, resulting in elevated CO concentrations in the flame zone and redistribution of radical pool from H to OH

- Conversely, some papers mistakenly attribute elevated CO concentrations to char gasification reaction or to thermal dissociation of CO_2 (unimportant until gas T > 2200 K)



Summary

An attempt has been made to clarify the (important) role of CO_2 in oxy-fuel combustion of pulverized coal:

- Most far-reaching impact is due to the much higher molar heat capacity of CO_2 (relative to N_2)
- The impact of radiantly active CO_2 on boiler-scale heat transfer is important
- Reduced gas diffusivity through CO_2 primarily influences pc char combustion
- CO_2 gasification reaction reduces char combustion T and slightly increases char consumption rate
- Reaction of H atom with CO_2 generates substantial quantities of CO in the flame zone

Acknowledgments

Funding provided by U.S. Department of Energy (DOE) Fossil Energy Cross-Cutting Research Program

Questions?